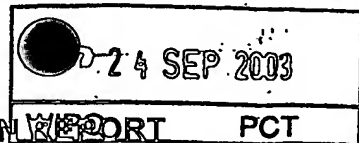


**INTERNATIONAL COOPERATION TREATY**  
**PCT**



**INTERNATIONAL PRELIMINARY EXAMINATION REPORT PCT**

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference <b>PJW:IHA:FP16873</b>		<b>FOR FURTHER ACTION</b>	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416).
International Application No. <b>PCT/AU03/00053</b>	International Filing Date (day/month/year) <b>20 January 2003</b>	Priority Date (day/month/year) <b>18 January 2002</b>	
International Patent Classification (IPC) or national classification and IPC <b>Int. Cl. <sup>7</sup> C23F 3/06, C23G 1/02</b>			
Applicant <b>CAST CENTRE PTY LTD et al</b>			

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.


2. This REPORT consists of a total of 5 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 4 sheet(s).

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☒ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☒ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand <b>8 August 2003</b>	Date of completion of the report <b>4 September 2003</b>
Name and mailing address of the IPEA/AU <b>AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustalia.gov.au Facsimile No. (02) 6285 3929</b>	Authorized Officer  <b>DAVID K. BELL</b> Telephone No. (02) 6283 2309

**I. Basis of the report****1. With regard to the elements of the international application:\***

- ☐ the international application as originally filed.
- ☒ the description, pages 4 to 6 & 8 to 22, as originally filed,  
pages 1 to 3 & 7, filed with the demand,  
pages , received on with the letter of
- ☒ the claims, pages 23 & 24, as originally filed,  
pages , as amended (together with any statement) under Article 19,  
pages , filed with the demand,  
pages , received on with the letter of
- ☒ the drawings, pages 1/11 to 11/11, as originally filed,  
pages , filed with the demand,  
pages , received on with the letter of
- ☐ the sequence listing part of the description:  
pages , as originally filed  
pages , filed with the demand  
pages , received on with the letter of

**2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.**

These elements were available or furnished to this Authority in the following language which is:

- ☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

**3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:**

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

**4. ☐ The amendments have resulted in the cancellation of:**

- ☐ the description, pages
- ☐ the claims, Nos.
- ☐ the drawings, sheets/fig.

**5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).\*\***

\* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).

\*\* Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report

**III. Non-establishment of opinion with regard to novelty, inventive step and industrial applicability**

1. The questions whether the claimed invention appears to be novel, to involve an inventive step (to be nonobvious), or to be industrially applicable have not been examined in respect of:

☐ the entire international application,

☒ claims Nos: **8, 9, 10, 16 & 17**

Because:

☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international preliminary examination (*specify*):

☐ the description, claims or drawings (*indicate particular elements below*) or said claims Nos. are so unclear that no meaningful opinion could be formed (*specify*):

☐ the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed.

☒ no international search report has been established for said claim Nos. **8, 9, 10, 16 & 17**

2. A meaningful international preliminary examination cannot be carried out due to the failure of the nucleotide and/or amino acid sequence listing to comply with the standard provided for in Annex C of the Administrative Instructions:

☐ the written form has not been furnished or does not comply with the standard.

☐ the computer readable form has not been furnished or does not comply with the standard.

**IV. Lack of unity of invention**

1. In response to the invitation to restrict or pay additional fees the applicant has:

- ☐ restricted the claims.
- ☐ paid additional fees.
- ☐ paid additional fees under protest.
- ☒ neither restricted nor paid additional fees.

2. ☐ This Authority found that the requirement of unity of invention is not complied with and chose, according to Rule 68.1, not to invite the applicant to restrict or pay additional fees.

3. This Authority considers that the requirement of unity of invention in accordance with Rules 13.1, 13.2 and 13.3 is

- ☐ complied with.
- ☐ not complied with for the following reasons:

4. Consequently, the following parts of the international application were the subject of international preliminary examination in establishing this report:

- ☐ all parts.
- ☒ the parts relating to claims Nos. **1 to 7, 11 to 15 & 18 to 20**

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement****1. Statement**

Novelty (N)	Claims 1 to 7, 11 to 15 & 18 to 20	YES
	Claims	NO
Inventive step (IS)	Claims 1 to 7, 11 to 15 & 18 to 20	YES
	Claims	NO
Industrial applicability (IA)	Claims 1 to 7, 11 to 15 & 18 to 20	YES
	Claims	NO

**2. Citations and explanations (Rule 70.7)**

D1 = Derwent Abstract Accession No. 38983X/21, JP 51-041639  
D2 = Derwent Abstract Accession No. 84-289020/47, DD 211811

The invention as defined in the present claims is a method of treating zirconium metal consisting of chemically de-passivating the zirconium metal

None of the cited documents either singly or obvious combination, disclose or fairly suggest the invention as defined in the present claims. The claimed invention is therefore novel and involves an inventive step. The claimed invention is industrially applicable.

## MAGNESIUM-ZIRCONIUM ALLOYING

### FIELD OF THE INVENTION

5 The present invention relates to the addition of zirconium to pure magnesium or magnesium alloys and to the preparation of magnesium-zirconium (Mg-Zr) alloys, including Mg-Zr master alloys.

### 10 BACKGROUND TO THE INVENTION

Zirconium is a potent grain refiner for magnesium alloys which contain negligible amounts of elements with which zirconium forms stable compounds, such as Al, Si, Fe, Ni,  
15 Co, Sn and Sb. Zirconium additions of about 1% by weight to such magnesium alloys can readily cause the grain size to decrease by 80% or more under normal cooling rates. The exceptional grain refining ability makes zirconium an important alloying element for magnesium alloys that are  
20 not based on alloying with Al and Si. For example, zirconium containing Mg-RE-Zn alloys such as EZ33 (Mg-3.3RE-2.7Zn-0.6Zr) and ZE41 (Mg-1.2RE-4.2Zn-0.7Zr) offer a specific combination of elevated temperature and room temperature properties which are not readily achievable  
25 with the Mg-Al-Zn alloys.

The solubility of zirconium in molten pure magnesium is approximately 0.6%, which slightly increases with increasing melt temperature. It has been reported that the  
30 most characteristic feature of the microstructure of a magnesium alloy that contains more than a few tenths per cent soluble zirconium is the zirconium-rich cores that exist in most of the magnesium grains. These zirconium-rich cores are believed to be the products of peritectic  
35 solidification. In order to achieve excellent grain refinement in commercial production, it is desirable to dissolve the full zirconium content (ie, about 0.6%) in a

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magnesium melt.

Over the decades various approaches to introducing zirconium into molten magnesium have been explored,

5 including:

- (a) alloying with different forms of zirconium metal;
- (b) alloying with zirconium sponge;
- (c) alloying with Zn-Zr master alloys;
- 10 (d) alloying with  $ZrO_2$ ;
- (e) alloying with various zirconium halides or complex halides or a mixture of halides and/or complex halides with different salts such as NaCl, KCl,  $BaCl_2$ , NaF, KF, etc; and
- 15 (f) alloying with Mg-Zr master alloys.

The advantages and disadvantages of each of these approaches have been discussed in detail by Saunders and Strieter (W. P. Saunders and F. P. Strieter, "Alloying  
20 Zirconium to Magnesium", Transactions of the American Foundrymen's Society, 1952, Vol. 60, pp. 581-594) and Emley (E. F. Emley, "Principles of Magnesium Technology", Pergamon Press, Oxford, 1966, pp. 127-155). Since about 1960, only Mg-Zr master alloys have been in  
25 widespread commercial use as sources of zirconium for alloying with magnesium. These Zr-rich Mg-Zr master alloys are generally made by chemical reduction by magnesium of salt mixtures based on zirconium fluorides or zirconium chlorides. A master alloy, developed by Magnesium Elektron  
30 Ltd (MEL) in about 1945 via chemical reduction of a complex zirconium fluoride by molten magnesium, has been long known as Zirmax (trade mark). A similar type of Mg-Zr master alloy was developed in the United States at about the same time based on a chloride salt reduction process.

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Zirmax type master alloys remain the primary zirconium alloying material used for the commercial production of zirconium-containing magnesium alloys. Zirmax contains approximately 33% zirconium and 67% magnesium and most of the zirconium is present as various sizes of zirconium particles (mostly in the range of submicron to 10  $\mu$ m) in a magnesium matrix.

Prior to Zirmax type master alloys becoming a standard source of zirconium for the production of zirconium-containing magnesium alloys, alloying with various forms of zirconium metal were investigated.

Sauerwald published work on alloying zirconium metal powder to magnesium in 1947 (V. F. Sauerwald, "*Dus Zustandsdiagram Magnesium-Zirkonnium*", Zeitschrift fur anorganische Chemie., 1947, Band 255, pp. 212-220). He added 5 wt% zirconium metal powder to magnesium under an argon atmosphere at various temperatures between 680 and 1100°C. Soluble zirconium contents exceeding 0.5 wt% (samples were digested in HCl acids) were obtained at all temperatures tested. In the same year, Ball reported work (C. J. P. Ball, "*Metallurgia*", 1947, Vol. 35, pp. 125-129; 211) stating that metallic zirconium dissolves in magnesium under an argon atmosphere at 900-1100 °C but that it was a difficult and costly process. Operating at such temperatures is not commercially feasible in view of vaporisation of magnesium. Emley reported in 1948 (E. F. Emley, "*Discussions of the Faraday Society*", 1948-49, Vol. 47, No. 4, pp. 219) that as zirconium metal powder is expensive and highly inflammable, it is natural to consider the possibility of alloying by a reducible zirconium compound.

In 1952, Saunders and Strieter reported their investigations in which different forms of metallic zirconium, (ie, zirconium sponge, fused zirconium, iodide-



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smaller than 3 microns, it can be readily suspended in a magnesium melt at the same temperature.

Chambers Science and Technology Dictionary (1991) defines  
5 "passivity" as "Lack of response of metal or mineral  
surface to chemical attack such as would take place with a  
clean, newly exposed surface. Due to various causes,  
including insoluble film produced by ageing, oxidation, or  
contamination; run-down of surface energy at discontinuity  
10 lattices; adsorbed layers..." Throughout this  
specification, the terms "depasivate", "depasivated" and  
"depasivating" are to be understood to have meanings  
derived from the foregoing definition of "passivity".

#### 15 SUMMARY OF THE INVENTION

In a first aspect, the present invention provides a method  
for treating zirconium metal, the method comprising  
chemically depasivating the zirconium metal. The  
20 zirconium metal is preferably zirconium sponge with the  
method forming treated zirconium sponge. The zirconium  
sponge may be chemically depasivated by treatment with a  
source of fluoride ions. The source of fluoride ions may be  
hydrofluoric acid. The source of fluoride ions may be  
25 a mixture of hydrofluoric acid and nitric acid.

The hydrofluoric acid preferably has a concentration  
between 0.1% and 50%, more preferably between 0.1% and 5%,  
and most preferably between 0.1% and 2.5%, with the acid  
30 concentrations calculated as shown later in this  
specification. These acid concentration ranges correspond  
respectively to about 0.05 - 25 molar, 0.05 - 2.5 molar  
and 0.05 - 1.25 molar. Efficacy at concentrations less  
than 0.1% HF, for example 0.07% (about 0.035 molar), has  
35 been demonstrated.